# 3 SEM TDC CHMH (CBCS) C 6

2022

( Nov/Dec )

### CHEMISTRY

(Core)

Paper: C-6

## ( Organic Chemistry )

Full Marks: 53
Pass Marks: 21

Time: 3 hours

The figures in the margin indicate full marks for the questions

- 1. Choose the correct answer from the following: 1×5=5
  - (a) Addition of HBr to 2-methylpropene in the presence of benzoyl peroxide mainly forms
    - (i) 1-bromobutane
    - (ii) 2-bromopropane
    - (iii) 2-bromo-2-methylpropane
    - (iv) 1-bromo-2-methylpropane

- The intermediate in the acid-catalyzed dehydration of alcohol is
  - (i) carbene
  - (ii) carbanion
  - (iii) carbocation
  - (iv) free adical
- electrophile involved (c) in the Reimer-Tiemann reaction is
  - (i) :CC12
  - (ii) <sup>⊕</sup>CHCl<sub>2</sub>
  - (iii) ĈHO
  - (iv) CCl<sub>3</sub>
- Malaprade reagent used to detect vicinal diol is
  - (i) OsO4
  - (ii) H<sub>5</sub>IO<sub>6</sub>
  - (iii) Pb(OAc)4
  - (iv) peracetic acid

- Which of the following compounds has the highest acid strength?
  - (i) C<sub>6</sub>H<sub>5</sub>OH
  - (ii) HCOOH
  - (iii) CH3COOH
  - (iv) CICH2COOH

#### UNIT-I

2. Answer any five of the following questions:

 $2 \times 5 = 10$ 

- (a) What is S<sub>N</sub>i mechanism? Explain with the help of an example.
- Discuss the benzyne mechanism for nucleophilic aromatic substitution reaction. Give evidences in support of the proposed mechanism.
- Synthesize the following:

 $1 \times 2 = 2$ 

- (i) Ethyl bromide by Hunsdiecker reaction
- (ii) Fluorobenzene through diazonium salt

- (d) Using organometallic compound, how would you prepare a 3°-alcohol from an ethyl ester?
- (e) Why are the aryl halides less reactive towards nucleophilic substitution reactions than alkyl halides?
- (f) Discuss the relative reactivity of alkyl, allyl and aryl halides towards nucleophilic substitution reactions.

#### UNIT-II

**3.** Answer any *three* of the following questions:

2×3=6

- (a) How will you distinguish between 1°-, 2°- and 3°-alcohols by Victor-Meyer method?
- (b) Complete the following reactions:

(i) 
$$CH_2OH + PCl_5 \longrightarrow ?$$

(ii) 
$$\left\langle \begin{array}{c} \\ \end{array} \right\rangle + H_2O + O \xrightarrow{\text{dil. alk. KMnO}_4} ?$$

- (c) How would you synthesize α,βunsaturated alcohol and aldehyde from glycerol?
- (d) Prepare acrolein from glycerol.
- **4.** Answer any *two* of the following questions:

3×2=6

(a) Complete the following reactions with mechanisms:

O—
$$CH_2$$
— $CH$ = $CHCH_3$ 
(ii)  $\longrightarrow$  (Claisen rearrangement)

- (b) (i) How can you prepare phenol from cumene? Give mechanism.
  - (ii) Give the mechanism of the following reaction:

(c) (i) Complete the following rearrangement and suggest the mechanism:

$$\begin{array}{c}
O \\
O \\
C \\
\hline
C \\
C
\end{array}$$
Anh. AlCl<sub>3</sub>

$$\begin{array}{c}
Anh. AlCl_3 \\
\hline
\Delta
\end{array}$$
(Fries rearrangement)

(ii) Complete the following reactions:

(1) 
$$CH_2$$
 + HCN  $\longrightarrow$  ?

(2) 
$$\stackrel{\text{CH}_2 \to \text{OH}}{\mid} \stackrel{\text{Pb(OAc)}_4}{\mid} \stackrel{\text{Pb(OAc)}_4}{\mid} ?$$

### UNIT-III

Answer either Q. No. 5 or Q. No. 6

**5.** (a) Complete the following reactions and write down the mechanisms:  $3\times2=6$ 

(Benzil-benzilic acid rearrangement)

(Continued)

(ii) 
$$+ Ac_2O \xrightarrow{AcONa}$$
 (Perkin reaction)

(b) Trichloroacetaldehyde is more reactive towards the nucleophilic addition reaction than acetaldehyde. Explain.

- **6.** (a) Explain with example the mechanism involved in Wittig reaction.
  - (b) Write one synthetic application of each of the following reagents (any three):

    1×3=3
    - (i) LiAlH4
    - (ii) Pb(OAc)4
    - (iii) NaBH<sub>4</sub>
    - (iv) PCC
  - (c) Write the Rosenmund's reaction for synthesis of acid chlorides.

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7. Answer any two of the following questions:

 $2 \times 2 = 4$ 

2

2

2

1

- (a) Synthesize the following (any one):
  - (i) Methylvinyl ketone from acetone
  - (ii) Crotonaldehyde from acetaldehyde
- (b) Write a short note on keto-enol tautomerism.
- (c) What is Michael reaction? Explain with a suitable reaction.
- **8.** How is barbituric acid prepared using malonic ester?

Or

Write any one preparation method of acetoacetic ester.

#### UNIT-IV

Answer either Q. No. 9 or Q. No. 10

9. (a) "Acetic acid is much weaker acid than formic acid." Explain.

(b) Identify A, B and C in the following reaction:

COOH  $\frac{\text{conc. HNO}_3}{\text{conc. H}_2\text{SO}_4} \rightarrow A \xrightarrow{\text{SOCl}_2} B$   $\frac{\text{NaBH}_4}{\text{H}_3\text{O}^+} \rightarrow C$ 

- (c) Synthesize the following:
  - (i) Propanoic acid to ethanoic acid by Hoffmann degradation
  - (ii) Butanoyl chloride to propanoic acid by Curtius rearrangement
- 10. (a) Arrange the following acids in increasing order of their relative acid strength with proper explanation:
  - (i) CH<sub>3</sub>-CH<sub>2</sub>-CH(Br)COOH
  - (ii) CH<sub>3</sub>-CH(Br)-CH<sub>2</sub>-COOH
  - (iii) CH<sub>2</sub>(Br)—CH<sub>2</sub>—CH<sub>2</sub>—COOH
  - (iv) CH3-CH2-CH2-COOH

3

 $2 \times 2 = 4$ 

2

(11)

(b) Show the mechanistic steps of the following reaction:

$$CH_3$$
— $C$ — $OC_2H_5 + H_2O$   $\stackrel{\text{H}^+}{=}$   $CH_3COOH + C_2H_5OH$ 

(c) Complete the following reactions (any two): 1×2=2

(i) 
$$COOH + 2CaO \xrightarrow{\Delta}$$

(ii) 
$$\begin{array}{c|c} \operatorname{CH_2COOH} & + \operatorname{SOCl_2} & \longrightarrow \end{array}$$
?

(iii) 
$$CH_2$$
—COOH  $H_2SO_4$  ?  $CH_2$ —COOH

(d) Account for the fact that maleic acid is a stronger acid than fumeric acid but maleate monoanion is a weaker acid than fumarate monoanion.

UNIT-V

Answer the following questions:

 $2 \times 2 = 4$ 

- 11. What are mercaptans? How will you prepare ethyl mercaptan from ethyl halide? 1+1=2
- 12. Give one method of preparation of thio-ether.

  What happens when a thiol reacts with an aldehyde in the presence of HCl?

  1+1=2

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